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Magnetic resonance measurements confirmed the fundamental pi-electron nature of the solitonic defect in polyacetylene. It is clear that the defect is delocalized with the exact extent and nature of delocalization dependent upon the lattice. For some polymer preparations, helium temperatures are required to freeze out dynamics and yield resolved ENDOR spectra. For these materials, the barriers to soliton delocalization must be small. Because of the dependence of ENDOR spectra upon polymer lattice, soliton concentration, and temperature, it is clear that the intrinsic (isolated chain) soliton localization/delocalization length cannot be obtained from the experimental data. The ratio of positive to negative spin densities appears not to change with polymer lattice implying that these are likely determined by intramolecular electron coulomb interactions. Most theoretical calculations are in reasonable agreement with the experimental numbers.

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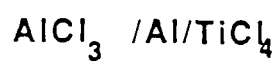
## FINAL TECHNICAL REPORT

## Development of Conducting Polymers of High Structural Strength

Our research can be divided into two parts according to chronology and focus. The first stage of our research program involved the investigation of prototype electroactive polymers such as polyacetylene, polythiophene, etc. The intention was to understand the fundamental nature of the charge carriers for electrical conductivity and the role of electron delocalization in defining optical and structural properties. Electron nuclear double resonance and electron spin echo studies were chosen as the microscopic probe of crucial electronic (soliton, polaron) states of the system. The objective was to identify the role played by various intra and intermolecular interactions in defining wavefunctions and state dynamics. The second phase of the research focused upon ladder polymers with the intent of realizing desired electronic and structural properties. The first detailed investigation of the electroactivity of traditional ladder polymers, BBL and BBB, was carried out and a vigorous program was undertaken to synthesize ladder polymers with desired electroactivity and which could be processed into desired forms such as thin films.

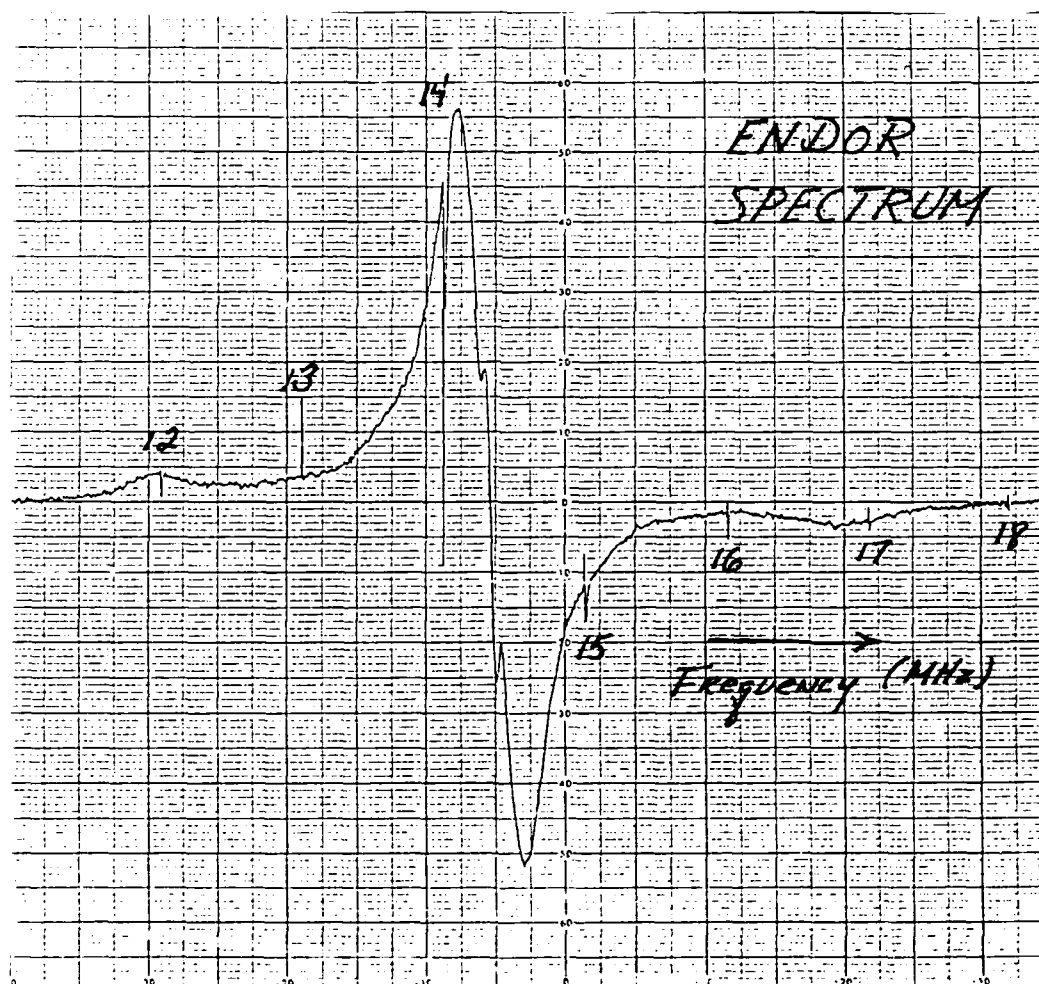
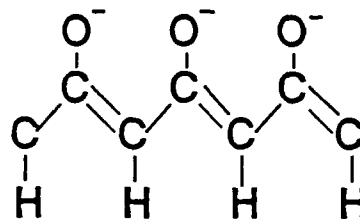
A crucial point of scientific focus and controversy has been the role played by solitonic and polaronic species in electrical conductivity. Central to understanding this role is the measurement of the extent of static and dynamic delocalization of these bond alternation defect states. Since solitons and polarons are paramagnetic it seems clear in hindsight that the logical way to define the defect wavefunction and dynamics is to employ electron nuclear double resonance and related techniques. ENDOR transition frequencies are linearly related to hyperfine interactions which are in turn directly related to defect spin densities at various nuclear positions. An ENDOR spectrum thus provides a map of a soliton or polaron wavefunction. The temperature dependence of the spectrum provides direct insight into defect dynamics. Realizing this, we carried out the first ENDOR measurements on the soliton defect in polyacetylene providing the first characterization of the soliton wavefunction. Multiple-ENDOR experiments were used to establish the existence of both positive and negative spin densities and the ratio of these define the magnitude of electron coulomb interactions. Unfortunately, our ENDOR measurements and those of other workers (which now reproduce all the features of our early measurements) have become the focal point of a bitter controversy over the exact shape of the soliton wavefunction and its precise extent of delocalization. The tragedy is that certain members of the scientific community fail to consider the data and realize that the points being debated are pointless. The debate focuses upon the exact form of the wavefunction and hence of the ENDOR spectrum. The important point to be noted experimentally is that the ENDOR spectra depend upon the nature of the polymer lattice (e.g., how the material was prepared) and upon temperature. Clearly, with a dependence upon lattice, it is meaningless to talk about the results being comparable to those computed for an isolated polymer chain. The important lesson for the community to learn from consideration of

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heptane/ethylene

140 C/ 18 hours



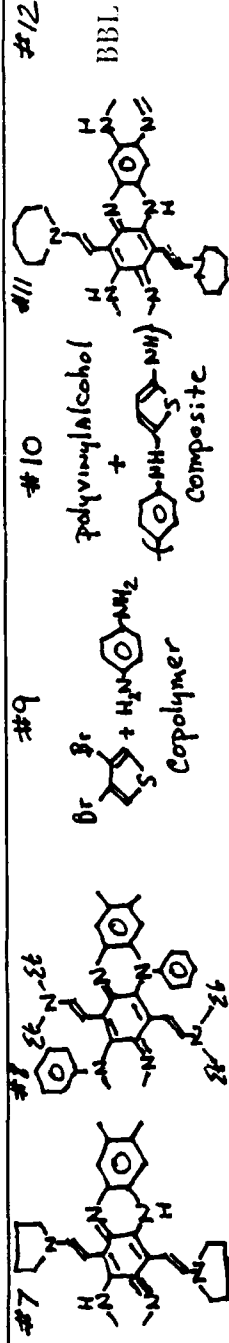
resonance measurements confirm the fundamental  $\pi$ -electron nature of this defect. Secondly, it is clear that the defect is delocalized with the exact extent and nature of delocalization dependent upon the lattice. For some polymer preparations, helium temperatures are required to freeze out dynamics and yield resolved ENDOR spectra. For these materials, the barriers to soliton delocalization must be small. Because of the dependence of ENDOR spectra upon polymer lattice, soliton concentration, and temperature, it is clear that the intrinsic (isolated chain) soliton localization/delocalization length cannot be obtained from the experimental data. The ratio of positive to negative spin densities appears not to change with polymer lattice implying that these are likely determined by intramolecular electron coulomb interactions. Most theoretical calculations are in reasonable agreement with the experimental numbers.

Highly ordered BBL and BBB films were prepared by processing from liquid crystalline solutions. We have carried out detailed electrical conductivity measurements over an extended range of temperatures for both pristine and chemically doped samples. Doping of samples by ion implantation has also been investigated. Conductivity has been investigated as a function of applied voltage and has been shown to arise from variable range hopping. By analysis of the highly anisotropic conductivity, we have been able to determine electron delocalization lengths both along the polymer backbone and normal to the polymer chain direction. On-chain electron delocalization extracted from the analysis of electrical conductivity data is found to be significantly greater than that determined from ENDOR measurements which likely reflects the different timescales involved in these two measurements. Delocalization lengths from ENDOR data appear to be more relevant to nonlinear optical data as is expected from the timescales of these two experiments. We have carried out degenerate four wave mixing (DFWM) measurements on BBL (see accompanying table) and have observed values quite comparable to those observed for polyacetylene. This is consistent with comparable electron delocalization lengths for the two samples determined from ENDOR measurements. Due to the nature of the liquid crystalline domains, light scattering (optical loss) is quite bad in the BBL samples.

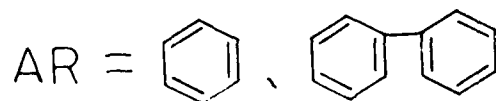
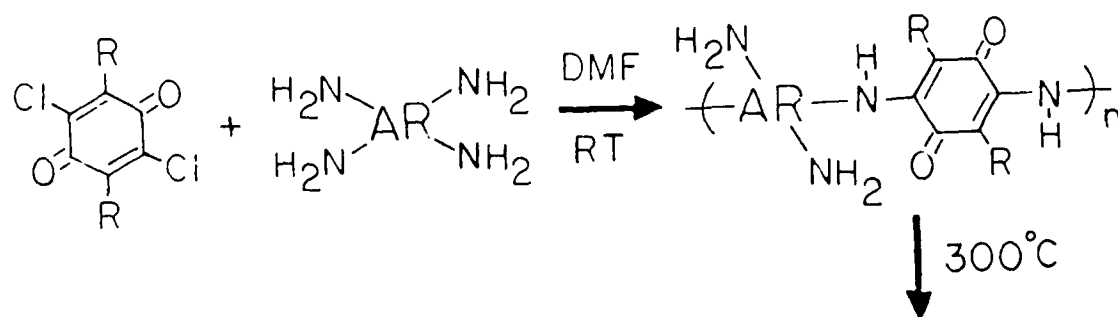
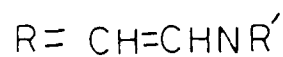
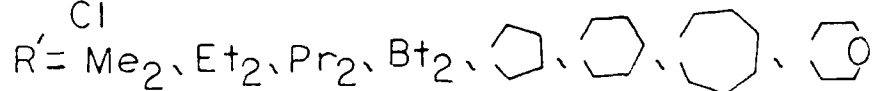
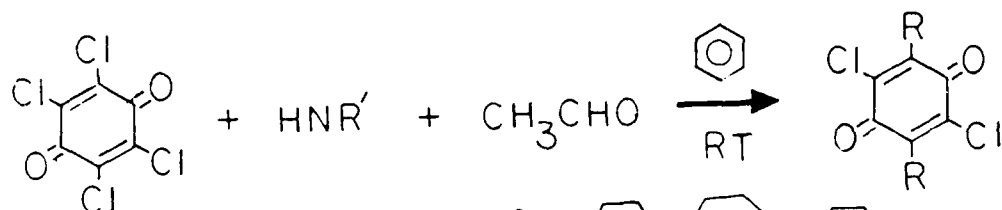
To avoid the harsh conditions (acid solvents and high temperatures) normally required for the preparation of ladder polymers, we developed dramatically different synthetic approaches to ladder polymers. An example of our approach is given in the accompanying figure and is characterized by the use of derivatization and soluble precursor polymer synthesis to prepared films of ladder polymers. The fundamental problem involved in the preparation of ladder polymer resides in the fact that the very delocalized  $\pi$ -electrons which give rise to electroactivity also promote strong polymer-polymer (Van der Waals) interactions. It is logical to use steric interactions associated with substituents to destabilize these polymer-polymer interactions. Solubility can also be enhanced by open-chain conformations which will an enhanced enthalpy of mixing and which are less suited for interchain  $\pi$ -electron interaction. As shown in the figure, it is logical to carry out the crucial processing operations at the open-chain precursor polymer stage and then convert to the final ladder

Table of optical and nonlinear optical data for representative polymers

Sample	#1	#2	#3	#4	#5	#6
n	1.96 ± 0.02	1.92 ± 0.02	1.92 ± 0.02	1.92 ± 0.02	1.92 ± 0.02	1.92 ± 0.02
$\alpha$ ( $\mu\text{m}^{-1}$ )	2.32 ± 0.16	3.57 ± 0.25	2.54 ± 0.18	2.3 ± 0.12	1.88 ± 0.13	4.08 ± 0.24
C <sub>1111</sub> ( $\times 10^{-10}$ esu)	9.8 ± 3.0	18.6 ± 5.0	8.9 ± 2.5	9.9 ± 3.1	7.4 ± 2.1	15.5 ± 5.1
C <sub>1221</sub> ( $\times 10^{-10}$ esu)	1.8 ± 0.5	2.8 ± 0.8	1.9 ± 0.5	2.2 ± 0.6	1.6 ± 0.5	3.0 ± 0.9
$\chi_t$ ( $\times 10^{-10}$ esu)	3.8 ± 1.2	9.3 ± 2.5	4.4 ± 1.2	4.0 ± 1.1	3.8 ± 1.2	7.7 ± 2.0
Sample	#7	#8	#9	#10	#11	#12
n	1.92 ± 0.02	1.82 ± 0.02	1.67 ± 0.02	1.58 ± 0.02	1.78 ± 0.02	
$\alpha$ ( $\mu\text{m}^{-1}$ )	1.89 ± 0.13	1.42 ± 0.14	0.93 ± 0.09	0.27 ± 0.01	0.91 ± 0.05	18.3
C <sub>1111</sub> ( $\times 10^{-10}$ esu)	8.0 ± 2.3	3.8 ± 1.2	2.3 ± 0.6	1.2 ± 0.3	3.6 ± 1.1	19.6
C <sub>1221</sub> ( $\times 10^{-10}$ esu)	1.4 ± 0.4	1.7 ± 0.5	1.3 ± 0.4	0.4 ± 0.1	1.1 ± 0.3	6.6
$\chi_t$ ( $\times 10^{-10}$ esu)	4.6 ± 1.4	3.6 ± 1.2	2.7 ± 0.8	0.5 ± 0.1	2.5 ± 0.8	



NEW SYNTHETIC ROUTE TO THE PREPARATION OF  
LADDER POLYMERS BASED UPON DERIVATIZATION AND  
SYNTHESIS OF OPEN-CHAIN PRECURSOR POLYMERS



structure by thermal processing. There are numerous other advantages to derivatization. For example, asymmetric derivatization can yield naturally amphiphilic molecules ideal for Langmuir-Blodgett techniques. Obviously, derivatization can be used to influence liquid crystalline phase behavior. We also note that derivatization can be used to influence electronic properties. For example, electron donating substituents can be used to stabilize polaron species. Studies supported under this grant focused upon utilization of alkyl and vinylamine derivatization to yield desired properties. Representative nonlinear optical data is given in the accompanying table. In addition to NLO measurements, a complete battery of conventional polymer characterization measurements, including elemental analysis, NMR, FTIR, mass spectroscopy, GPC, TGA, DSC, TMA, etc. were carried out. Defects which limit optical nonlinearity have been identified. The most serious of these appears to be incomplete condensation and air oxidation of imine nitrogens (see accompanying figure).

A detailed theory for the quantitative analysis of the degenerate four wave mixing experiment has been developed. This theory which explicitly takes into account the polarization and pulse profiles of the incident beams permits extraction of complete tensorial information. Electronic, thermal, and acoustic components of the DFWM signal can be quantitatively deconvolved. A number of interesting observations have been made on ladder polymers. First of all, it can be noted that the laser damage threshold is quite high, typically on the order of 1 GW/cm<sup>2</sup>. Secondly, it can be noted that no saturation of the optical nonlinearity is observed before damage; this implies that the response is nonresonant even though the measurement is made at a frequency where optical loss (absorption) is occurring. This situation is obviously dramatically different than typically observed for inorganic materials where absorption and third order susceptibility are typically correlated. The answer to the dilemma may reside in the fact that organic materials are characterized by both localized and delocalized states. These are expected to contribute quite differently to optical nonlinearity. For ladder polymers a number of transitions ( $\pi$ - $\pi^*$ ,  $n$ - $\pi^*$ , exciton) may be nearly degenerate. Moreover, new mechanisms (involving mid-gap polaron states) may be operative.

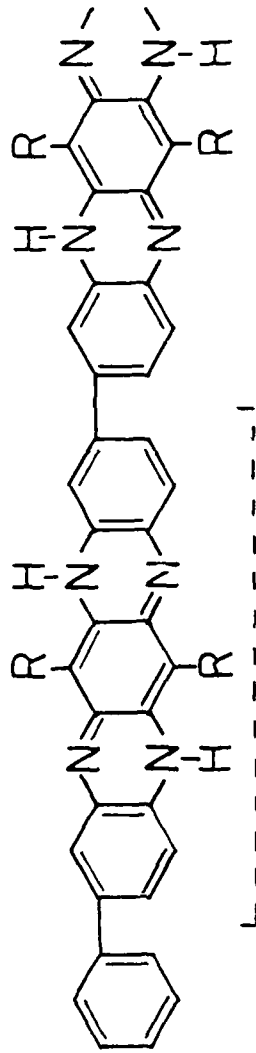
One theoretically predicted trend that is clearly observed in the experimental third order susceptibility data is the increase observed in going from open chain precursor polymer to fully fused ring ladder polymer. Due to steric interactions, a nonplanar conformation applies in the open chain precursor polymer (i.e., a nonzero dihedral angle between adjacent phenyl rings). Thus,  $\pi$ -orbital overlap is less optimum in the open chain polymer than in the fused ring ladder polymer. This trend is consistently predicted by the theoretical calculations of Medrano of the Air Force Wright Aeronautical Laboratories.

Both electronic and thermal components of the DFWM signal depend upon the nature of the vinylamine substituents. Correlation of third order susceptibility data with NMR data suggests that the correlation derives from electron donation from the substituent to the  $\pi$  system of the polymer backbone.



STRUCTURAL FACTORS (IMPERFECTIONS) LIMITING  
OPTICAL NONLINEARITY IN LADDER POLYMERS

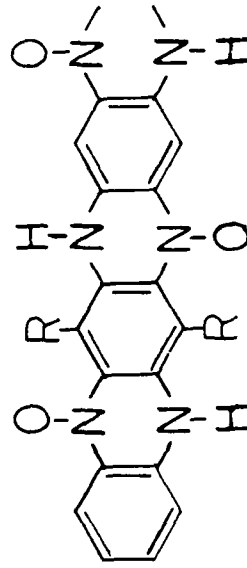
$\chi$   
(esu)  
 $2 \times 10^{-9}$



NONPLANAR  
CONFORMATION  
SEGMENT

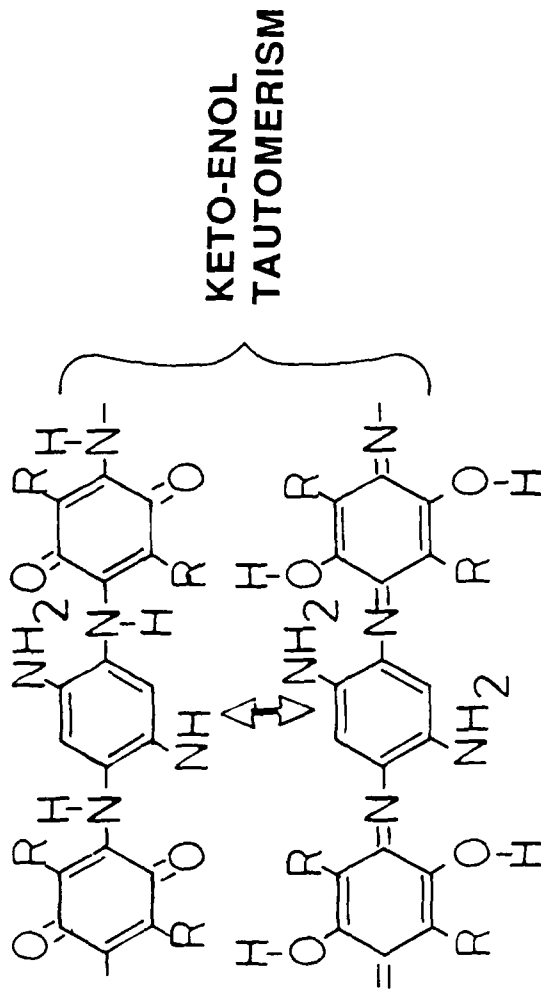
AIR OXIDATION OF  
IMINE NITROGENS

$4 \times 10^{-11}$

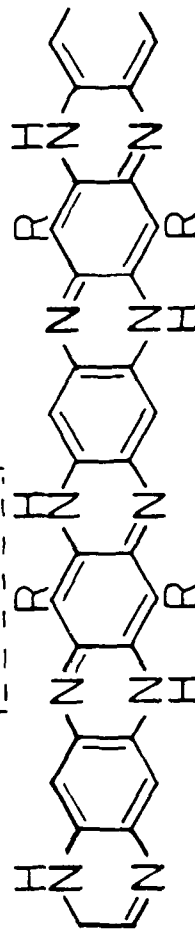


INCOMPLETE  
CONDENSATION

$1 \times 10^{-10}$



IDEAL STRUCTURE  
(NOT YET REALIZED)



?

Whether the mode of action is the stabilization of mid-gap polaron states is not known at this time.

In addition to derivatized ladder polymers, a variety of related polymers have been synthesized. For example, we have prepared copolymers of polythiophene and polyaniline and have characterized the nonlinear optical as well as physical properties of these materials. We have also succeeded in preparing composites of these copolymers with polyvinylalcohol. Third order susceptibility data for the copolymer and composites are summarized in the accompanying table.

## COMPLETED PROJECT SUMMARY

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GRANT NUMBER: F49620-85-C-0096

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"Evidence for Soliton-Phonon Interaction in trans-Polyacetylene: Temperature and Frequency Dependence of Electron Spin-Lattice Relaxation Data," B H Robinson, J M Schurr, A L Kwiram, H Thomann, H Kim, A Morrobel-Sosa, P Bryson, and L R Dalton, J Phys Chem, **89**, 4994 (1985)

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"Dielectric Properties of Copper Phthalocyanine Polymers," H S Nalwa, L R Dalton, and P L Vasudevan, Eur Polym J, **21**, 943 (1985)

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"The Role of Extensively Delocalized  $\pi$ -Electrons in Electrical Conductivity, Non-Linear Optical Properties and Physical Properties of Polymers," L R Dalton, J Thomson, and H S Nalwa, Polymer, **28**, 543 (1987)

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"Electroactive Polymers: Consequences of Electron Delocalization," L R Dalton, Nonlinear Optical and Electroactive Polymers (P N Prasad and D R Ulrich, eds), Plenum, New York, 243 (1987)

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"Synthesis and Characterization of New Electroactive Polymers," L P Yu and L R Dalton, Synthetic Metals, in press

"Optical, Magnetic Resonance, and Conductivity Studies of the Ladder Polymer BBL," F Coter, Y Belaish, D Davidov, L R Dalton, E Ehrenfreund, M R McLean, and H S Nalwa, Synthetic Metals, in press

"Synthesis of New Soluble and Processible Electroactive Polymers," L P Yu and L R Dalton, Progress in Rubber and Plastics Technology: Proceedings of the 1st International Conference on Electrical, Optical, and Acoustic Properties of Polymers, The Plastics and Rubber Institute (1988)

"Synthesis of New Nonlinear Optical Ladder Polymers," L R Dalton, Nonlinear Optical Effects in Organic Polymers (J Messier, F Kajzar, P N Prasad, and D R Ulrich, eds) NATO ASI Series No. 971 (1988)

"Observation and Analysis of Soliton Localization in Durham Polyacetylene," L R Dalton, A I Vistnes, J Thomson, C Johnston, H Thomann, and B M Hoffman, submitted to J Phys Chem

"ESE Studies of Oxygen Effects in Polyacetylene," A Morrobel-Sosa and L R Dalton, submitted to J Phys Chem

#### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

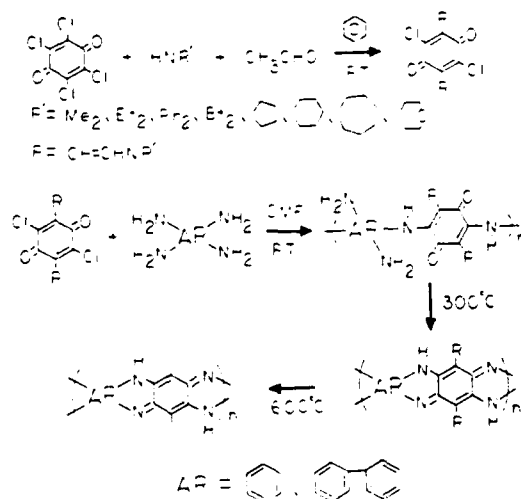
The first objective of this research was to realized an improved understanding of electrical, magnetic, and optical properties in high symmetry polymers capable of supporting significant  $\pi$ -electron delocalization. The second objective was to develop new synthetic approaches for the preparation of soluble electroactive polymers and to process these materials into forms appropriate for exploitation of their unique properties.

The project consisted of three parts. The first part focused on defining fundamental bond alternation defects (solitons and polarons) in prototype conducting polymers such as polyacetylene, polythiophene, etc. Accomplishments include the first ENDOR measurements on these materials which in turn provided the first quantitative definition of the extent and shape of the wavefunction of such defects. ENDOR and TRIPLE measurements also provided the first measurement of electron coulomb interactions, a quantity which together with electron phonon interaction determines electron localization/delocalization in  $\pi$ -electron polymers. Subsequently, these measures of electron localization/delocalization were correlated with quantities, such as third order nonlinear optical susceptibility, which are theoretically predicted to depend upon electron delocalization.

The second area focused upon defining the optical, magnetic, and electrical properties of the well-known ladder polymers BBL and BBB. For example for BBL, our optical studies indicate a interband  $\pi$ - $\pi^*$  gap of approximately 1.8 eV

in the neutral undoped state and the presence of charged defects which increase in number upon doping. Electron paramagnetic resonance and ENDOR studies suggest that these defects are polarons. A highly anisotropic conductivity is observed over the temperature range 300-700 C which could be fit to Mott's model of variable range hopping. The conductivity anisotropy is attributed to anisotropic localization lengths of the localized states. Electron delocalization defined from the analysis of electrical conductivity data is considerably greater than that defined by ENDOR measurements. This disagreement can likely be attributed to the different timescales involved in the two experiments. ENDOR data are more appropriate for correlation with short timescale phenomena such as nonlinear optical activity. A third order susceptibility of approximately  $2 \times 10^{-9}$  esu was measured by degenerate four wave mixing at 532 nm for a BBL sample characterized by a linear absorption of 18  $\mu\text{m}^{-1}$  and an index of refraction of 2.3. The reversibility of BBL to thermal cycling over the temperature range 300-700 C was investigated; heating of the as-synthesized polymer results in decarbonylation and a subsequently thermally stable lattice.

A major research activity has been the synthesis of soluble electroactive polymers by derivatization and soluble precursor polymer methods. Of particular focus has been the synthesis of polyquinoxaline ladder polymers by such techniques. Ladder polymers were chosen for extensive investigation because they exhibit a molecular conformation optimizing  $\pi$  orbital overlap, hence, electron delocalization. Polycondensation synthesis was pursued to permit synthesis of oligomeric model compounds and to facilitate soluble precursor polymer synthesis by careful control of the asymmetric condensation process. Asymmetric derivatization has permitted the preparation of naturally amphillic oligomers and polymers which have been utilized with Langmuir-Blodgett processing methods to prepare ordered films. Derivatization also influences liquid crystalline properties and ordered films have been processed from liquid crystalline solutions. An example of the preparation of derivatized ladder polymers is shown in the accompanying figure.



The optical nonlinearity of the vinylamine-derivatized polymers shown in this figure have been investigated by degenerate four wave mixing with third order susceptibilities in the range  $10^{-9}$  to  $10^{-11}$  esu typically observed for pristine polymers. Nonlinear optical data was correlated with extensive analytical data including elemental analysis, NMR, FTIR, mass spectroscopy, UV-Vis, TGA, DSC, and chromatography data. Electron delocalization and optical nonlinearity appear to be limited by polymer imperfections associated either with incomplete condensation or air oxidation of imine nitrogens. Comparison of optical nonlinearity data for open-chain precursor polymers with data for fully-fused ring ladder polymers permits insight into the dependence of electron delocalization and optical nonlinearity on molecular conformation. The enhanced susceptibilities observed for ladder polymers are in agreement with preliminary theoretical calculations. Both electronic and thermal components of the third order susceptibility are observed to depend upon the nature of the vinylamine substituent. Finally, we note that, in addition to homopolymers, we have prepared a variety of copolymers and composite materials.